Propagation of Errors in Evironmental Measurements

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Importance of Error Analysis

- How accurate are the data? Do I care?
- Data -------> Decisions
  - Are the data good enough?
  - How do I know if data are good enough?
- Data of unknown quality are next to useless.

Example

- Is 12 ppm > 10 ppm?

  No, 12 ± 5 ppm $\ngtr$ 10.0 ppm at 95% confidence level.

- Is 10.2 ppm > 10 ppm?

  Yes, 10.2 ± 0.1 ppm > 10.0 ppm at 95% confidence level.

Data of unknown quality cannot be compared.

Type of Errors

- **Systematic Errors:** Always same sign and magnitude and produce biases.
- **Random Errors:** Vary and unpredictable in sign and magnitude.
- **Blunders:** Simply mistakes that occur on occasion and produce erroneous results.

Detectable Errors

Errors can be detected by a data reviewer:

- **Planning errors**
- **Sampling or field errors**
- **Analytical or lab errors**
- **Reporting errors**

Nondetectable Errors

Errors cannot be detected by a data reviewer:

- Random errors
- Indeterminate errors
  - Analyte loss to container
  - Sample contaminations
  - Undocumented change of sampling coordinates

Detection of Errors

- **Apply common sense**
  - Do data look suspicious?
  - Are data internal consistent?
  - Were plans/procedures properly adapted?
- **Compare data with criteria and background**
  - Laws and regs.
  - Plans and SOPs
  - Results and reports
  - Site description

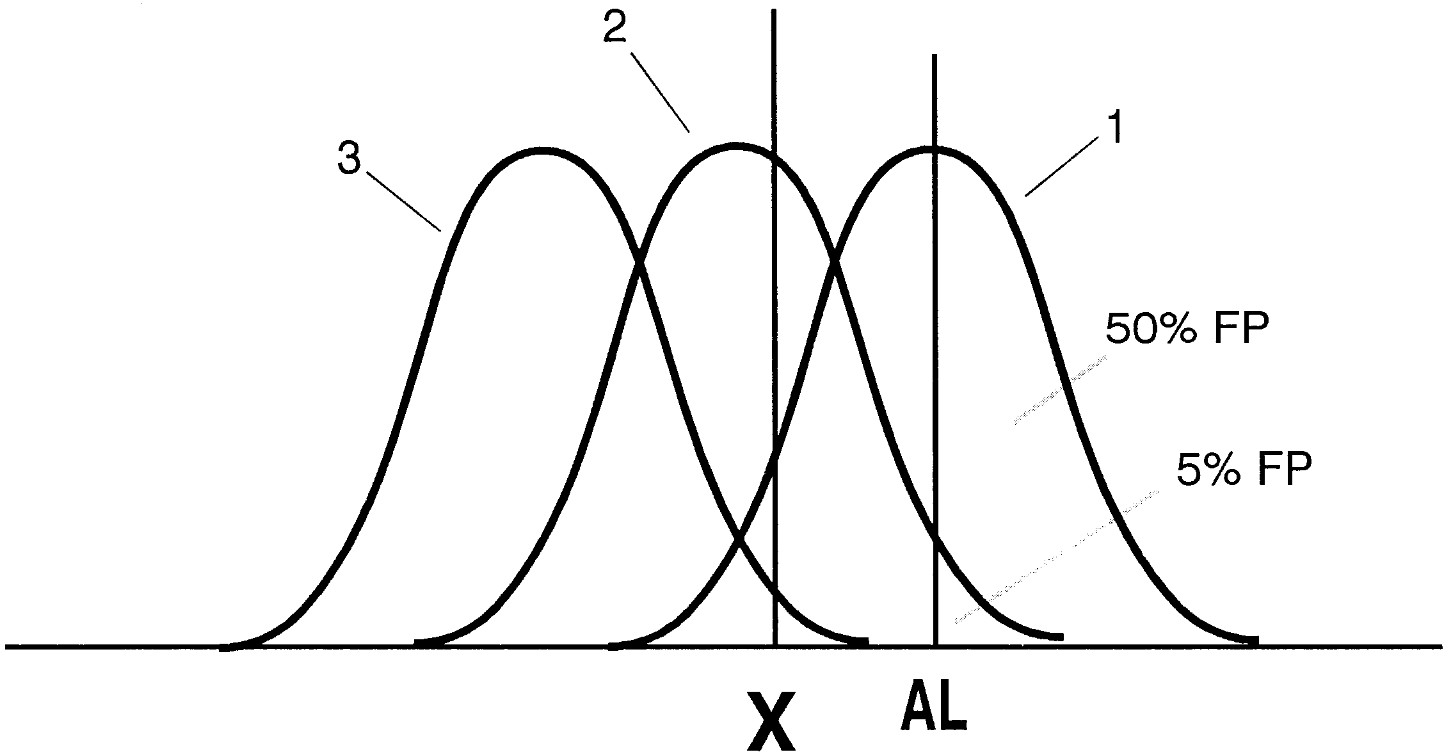
Features of Environmental Chemical Analysis

- Single discrete or composite sample
- Large number of target analytes
- Complicated sample matrices
- Limited method performance data
- Method QCs are appropriate for controlling and describing method performance for samples of similar matrices.
- Decision might be based on comparison of data of vague quality with action levels.

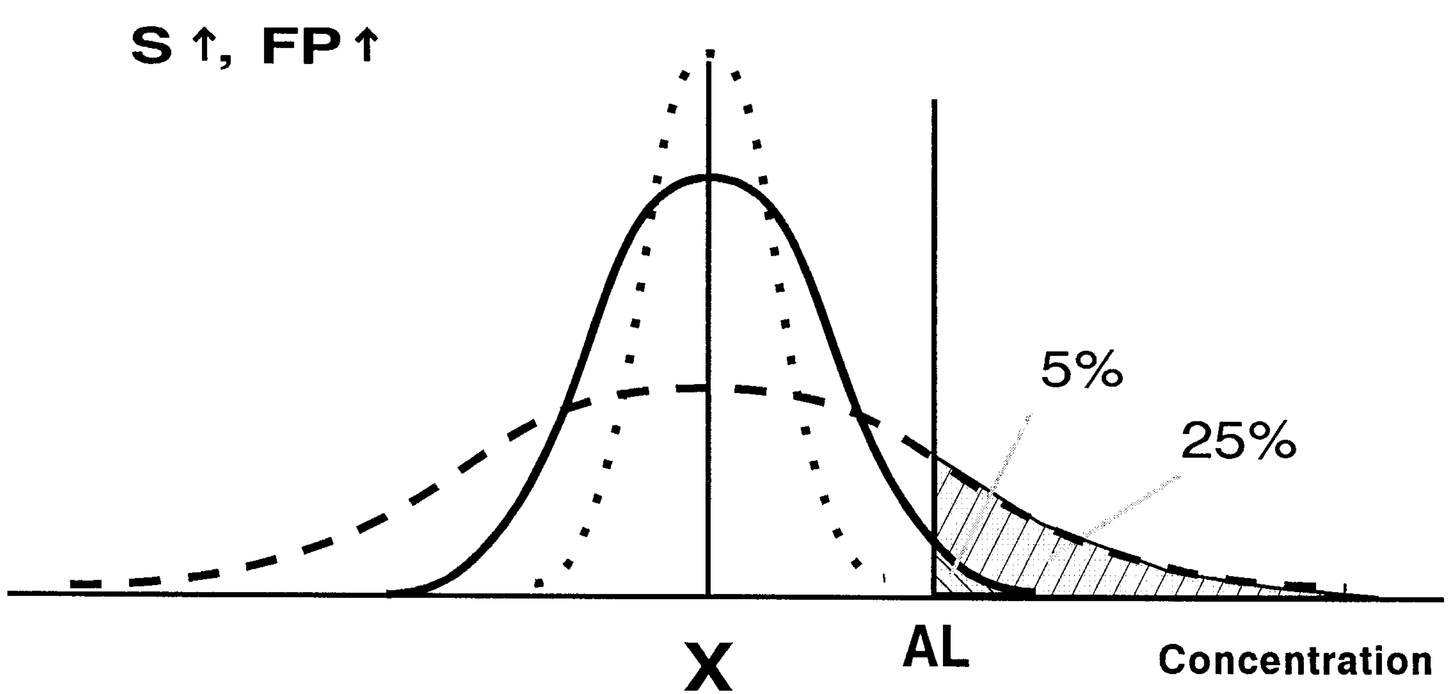
Error Analysis

- DQO ---> MQO ---> DQI
- MQO: Data Validation ---> PARCC
- DQI: MDL, Bias, and Precision
- Field Sampling Errors and Lab Errors

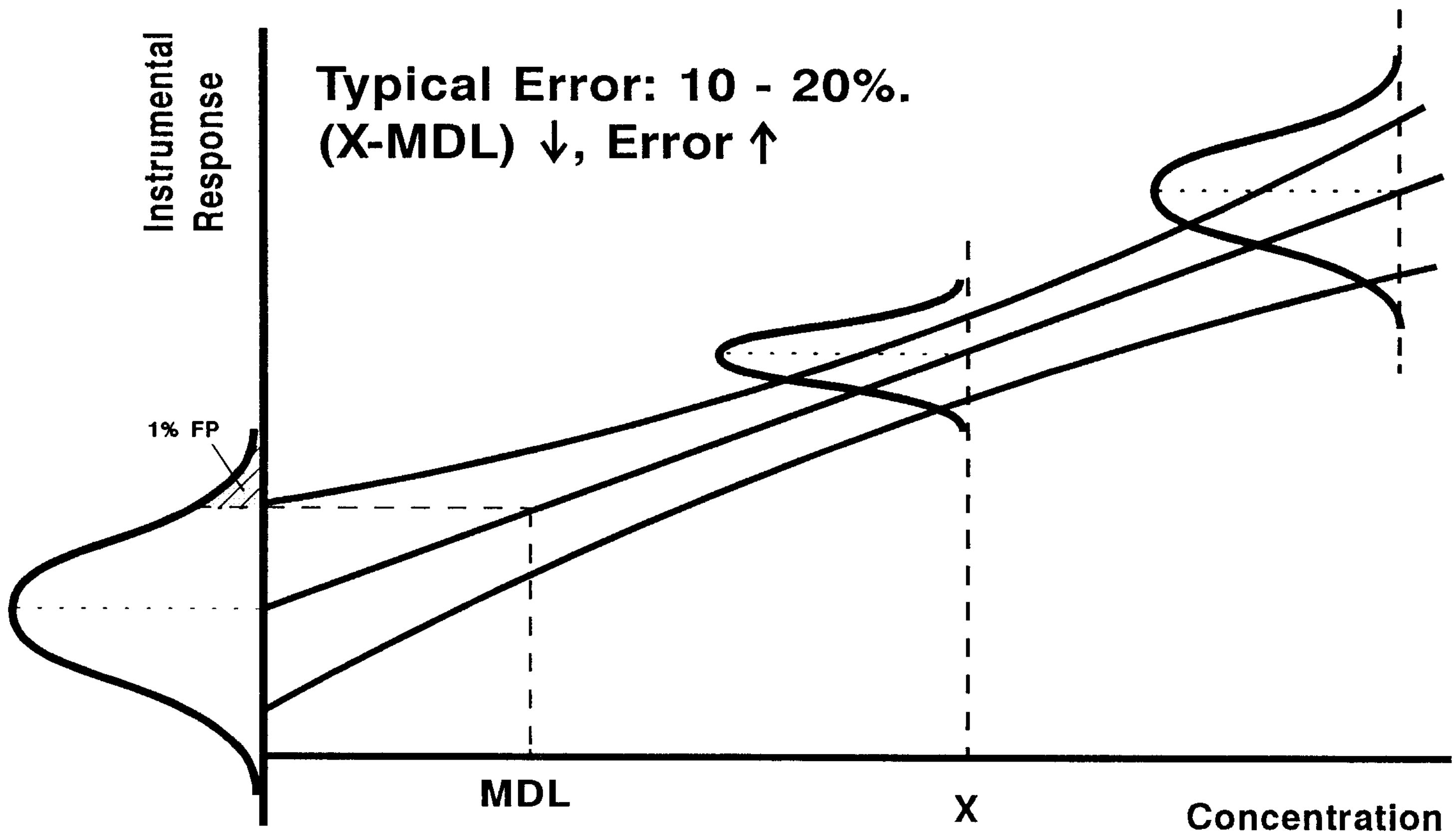
Decision Errors



Acceptable Decision Errors



Analytical Errors



MDL and MQL

1. MDL: 40 CFR 136, Appendix B; 7 replicates in a clean or sample matrix.

2. MDL Check Samples: 2 times MDL on a quarterly basis.

3. Uncertainty: $\approx \pm(100 \div n)\%$ for analytes at concentrations of n times MDLs.

4. MQL: 5 - 10 times MDL depending on calibration error.

Control Charts

1. Establish control limits for all LCSs based on a minimum of 40 data points and demonstrate that a lab is under statistical control.

2. Shell: Control and report data quality based on LCS control limits.

3. Default LCS control limits (Also refer Method Compendium):

   Organics: %R = 30 - 150%; %D = ≤ 40%.
   Inorganics: %R = 70 - 130%; %D = ≤ 25%.

4. Published limits shall be used if tighter, and lab shall demonstrate their performance.

Sampling Errors

- Pierre Gy's "Sampling Theory and Sampling Practice."
- Overall Error = Field Sampling Errors + Lab Errors
- Field Sampling Errors
  - Fundamental Error (FE)
  - Grouping and Segregation Error (GE)
- Lab Errors
  - Sample Preparation Error (PE)
  - Analytical error (AE)

Field Sampling Errors

- **Fundamental Error (FE):**
  - Resulted from constitution heterogeneity of samples.
  - Always there even with perfect sampling.
  - Approximately half of sampling error.
  - The only error that can be estimated.

- **Grouping and Segregation Error (GE):**
  - Resulted from distribution heterogeneity of samples.
  - Assumed to be equal to the FE.
  - All sample preparation efforts are designed to minimize this error.

Fundamental Error

The relationship between fundamental errors (FE), sample size, and particle size is:

S = (18 * f * e * d ^ 3 / Ms) ^ (1/2)

$$S = (18 \cdot f \cdot e \cdot d^3 / M_s)^{1/2}$$

where

S: RSD of analyte concentration due to FE.
f: dimensionless factor of particle shape.
e: average density, assumed to be 2.5 g/cc.
d: the diameter of the largest particle in cm
Ms: the mass of sample in gram.

Fundamental Error

"f" factor for different particle shapes

Particle Shape	f
Cubic	1
Spheres	0.5
Flakes	0.1
Needles	>1 to ≤10
Soft solids shaped by mechanical stress	0.2

Fundamental Error

Assuming spherical soil particles, the largest particle size that can be representatively accommodated by a given subsample mass and given fundamental error can be calculated as follows.

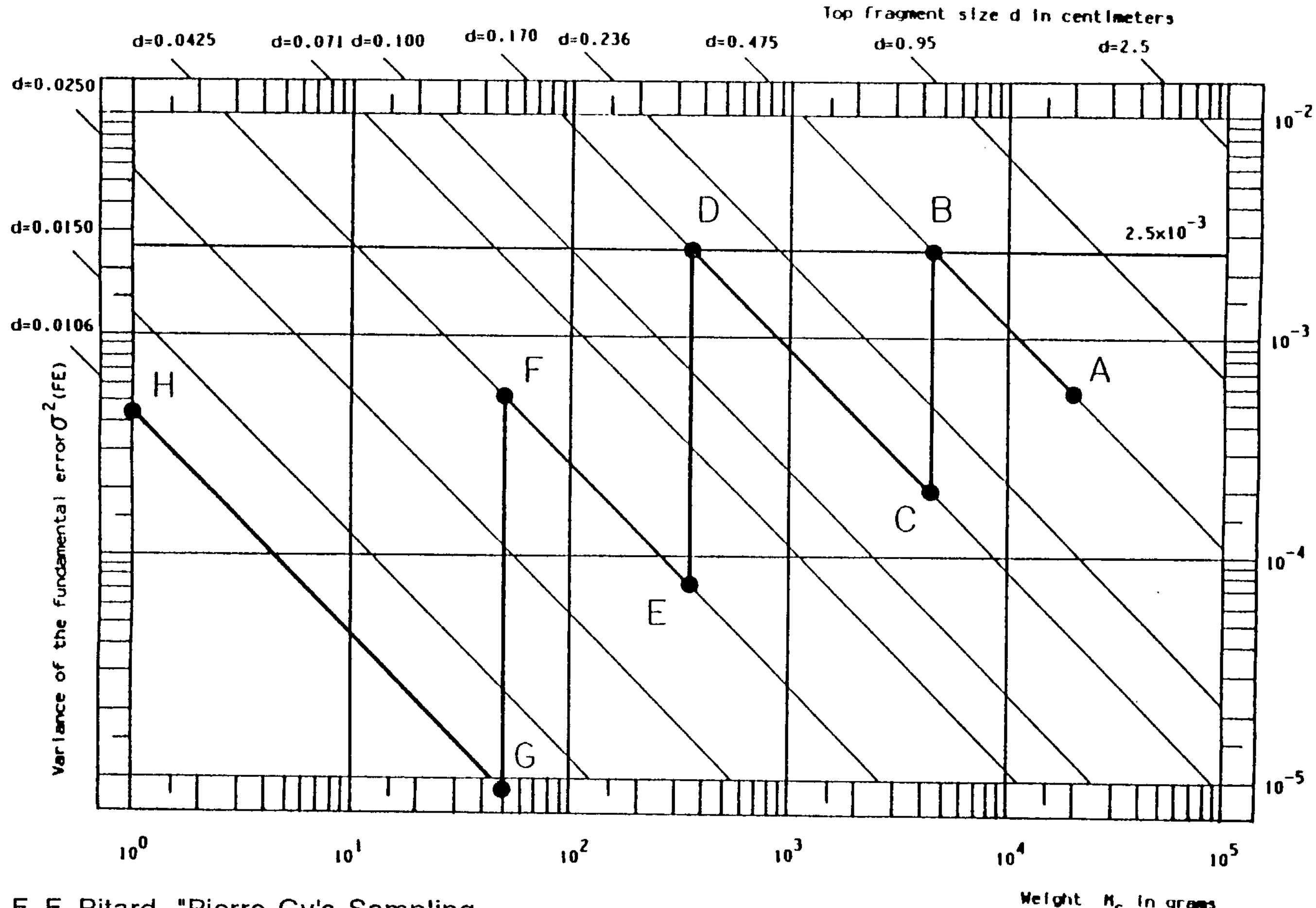
$$d = (Ms * S^2 / 22.5)^{(1/3)}$$

Sample Mass (g)	Sieve Size	particle size (cm) 5%RSD	10%RSD	15%RSD
0.1	35	0.02	0.04	0.05
1	18	0.05	0.08	0.10
2	13	0.06	0.10	0.13
5	12	0.08	0.13	0.17
10	10	0.10	0.16	0.22
50	6	0.18	0.28	0.37

Fundamental Error

- Rule of thumb ---> "S(FE) < 15%" (as %RSD)
- If the diameter of the largest particle in the soil to be sampled is known, the sample weight controls the FE.
  - If d = 0.8 cm, for a 100 g sample, S(FE) = 34%
  - If d = 0.8 cm, for a 500 g sample, S(FE) = 15%
  - when sampling this soil media, samples should exceed 500 g.

Fundamental Error



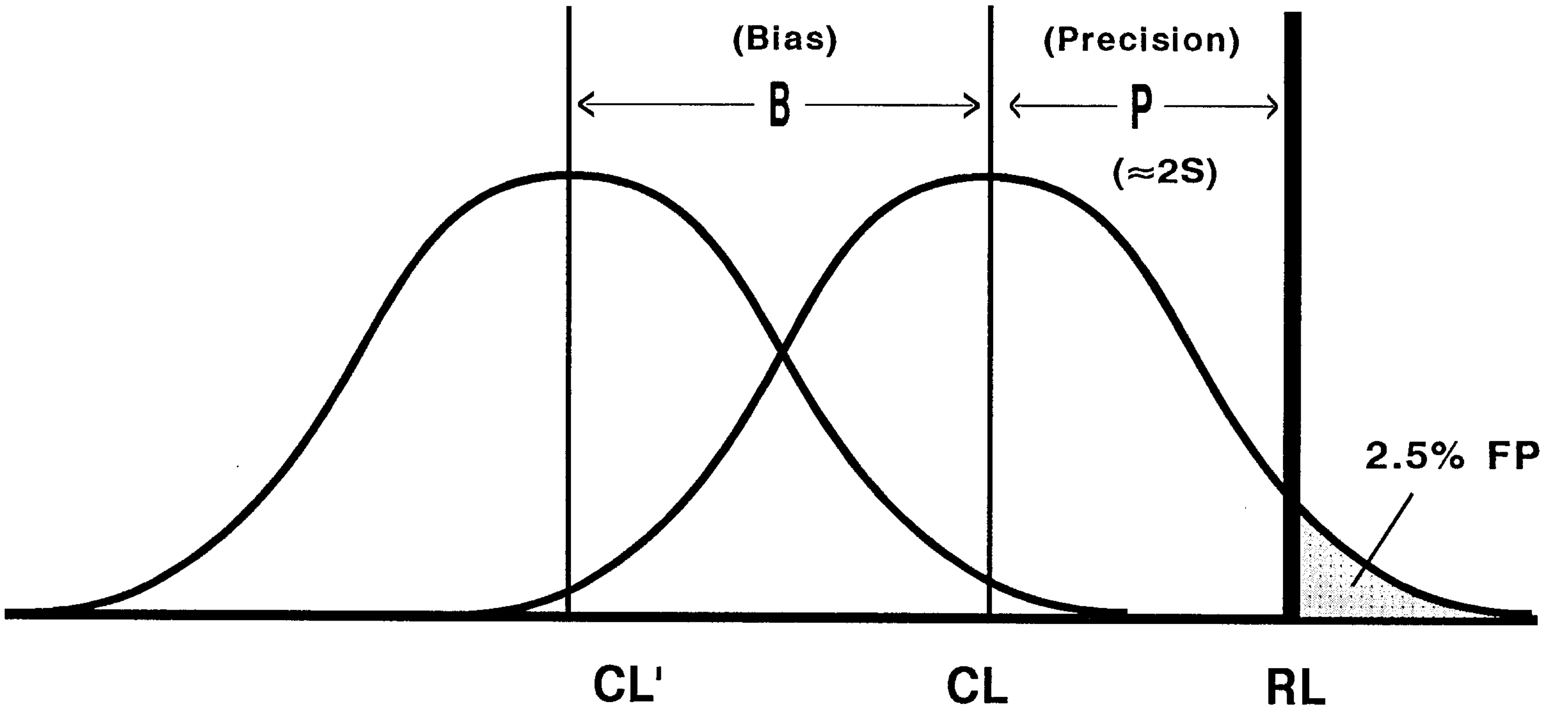
Source: F. F. Pitard, "Pierre Gy's Sampling Theory and Sampling Practice"

Lab Errors

- **Sample Preparation Error (PE):**
  - Potentially the largest and most often neglected error.
  - To minimize, reduce particle size and heterogeneity.
- **Analytical Error (AE):**
  - Generally the smallest error when lab is in control, but the greatest amount of money and effort in project QC is focused on.
  - To minimize, use GLP and QA/QC.

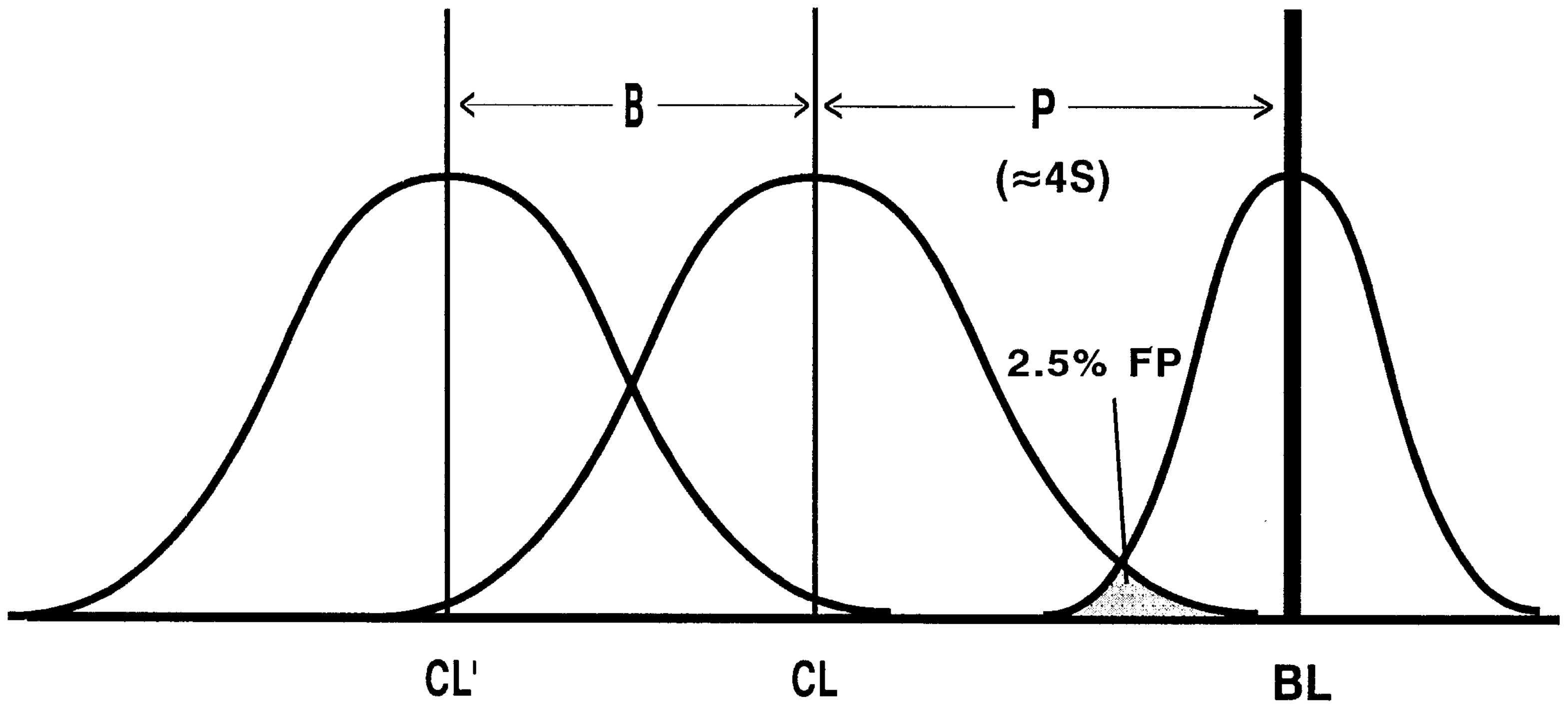
Comparison with Reg. Level

If FP $\leq$ 2.5%, B = -20%, P = $\pm$10%



Comparison with Bkgd. Level

If FP ≤ 2.5%, B = -20%, P = ±30%



Conclusions

- A simple process to assess sampling and analysis errors. (Allocating 75% of data budget to reduce analytical error from 25% to 15% is not fruitful if the sampling error is 80%.)
- A consistent way to express method performance and data quality in quantitative terms.
- A straightforward approach to select appropriate methods and generate data of known and adequate quality.